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AN INVESTIGATION OF THE DYNAMICS
OF THE ELECTROLYTE DISTRIBUTION SYSTEM
IN THE PS502-502A POWER SUPPLY

Glenn L. Scillian

Conant H. Emmons

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DIAMOND ORDNANCE FUZE LABORATORIES
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FOR THE COMMANDER:
Approved by



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Chief, Laboratory 300

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ABSTRACT

The motion of the pumping diaphragm in the electrolyte reservoir of the PS502-502A power supply was studied during its operation by means of transparent models and high-speed motion picture photography. The primary purposes of the investigation were to determine the causes of occasional diaphragm failure that has led to electrical failure of the battery and to find means of eliminating the causes. The failures were found to be due to excessive mechanical stress caused, in turn, by (1) high-pressure shock from the detonating squibs used to release the stored pressurized gas and (2) improper folding of the diaphragm during activation. Recommendations are given for the improvement of design and performance.

1. INTRODUCTION

To assure an extended shelf life, the silver-oxide zinc battery must be kept dry, i.e., the electrolyte must not wet the electrodes. Consequently, the cells must be capable of being filled with electrolyte just prior to use. The PS502 and PS502A* power supplies (ref 1)** contain a mechanism for the automatic transportation of the electrolyte from its storage to the cell pack. The electrolyte reservoir has the shape of an ellipsoid of revolution about its minor axis. The reservoir consists of three main parts: the upper and lower halves of stainless steel and a thin silver diaphragm that divides the cavity into two parts (fig. 1). Initially the diaphragm rests against the inner surface of the upper half, allowing the total volume of the reservoir to be filled with electrolyte. Upon activation, pressurized gas enters the space between the upper reservoir half and the diaphragm. The pressure, transmitted through the electrolyte, ruptures a seal at the center of the lower half, and pushes the electrolyte through a heat exchanger into the cell pack. The reservoir, with its diaphragm, acts as a one-stroke pump as the flexible diaphragm inverts, follows the electrolyte, and finally comes to rest against the inner surface of the lower half of the reservoir.

This reservoir design was developed in 1954 by DOFL and the American Machine and Foundry Company, Raleigh, N. C.*** The design has several important advantages: (1) it contains no sliding parts; (2) it offers a chemically inert, all-metal storage space for the potassium hydroxide electrolyte, and (3) theoretically, at least, it requires no stretching of the diaphragm. The diaphragm should fold through a circle of increasing diameter concentric with the reservoir axis, without wrinkles.

Recent tests have shown that the diaphragm does not fold from the center, but from one edge (at the gas inlet point) and then from the

* PS502 - Ordnance part no. 1043654

PS502A - Ordnance part no. 10404920

** List of references appears on page 31.

*** Now Missile Battery Division of Electric Storage Battery Company.

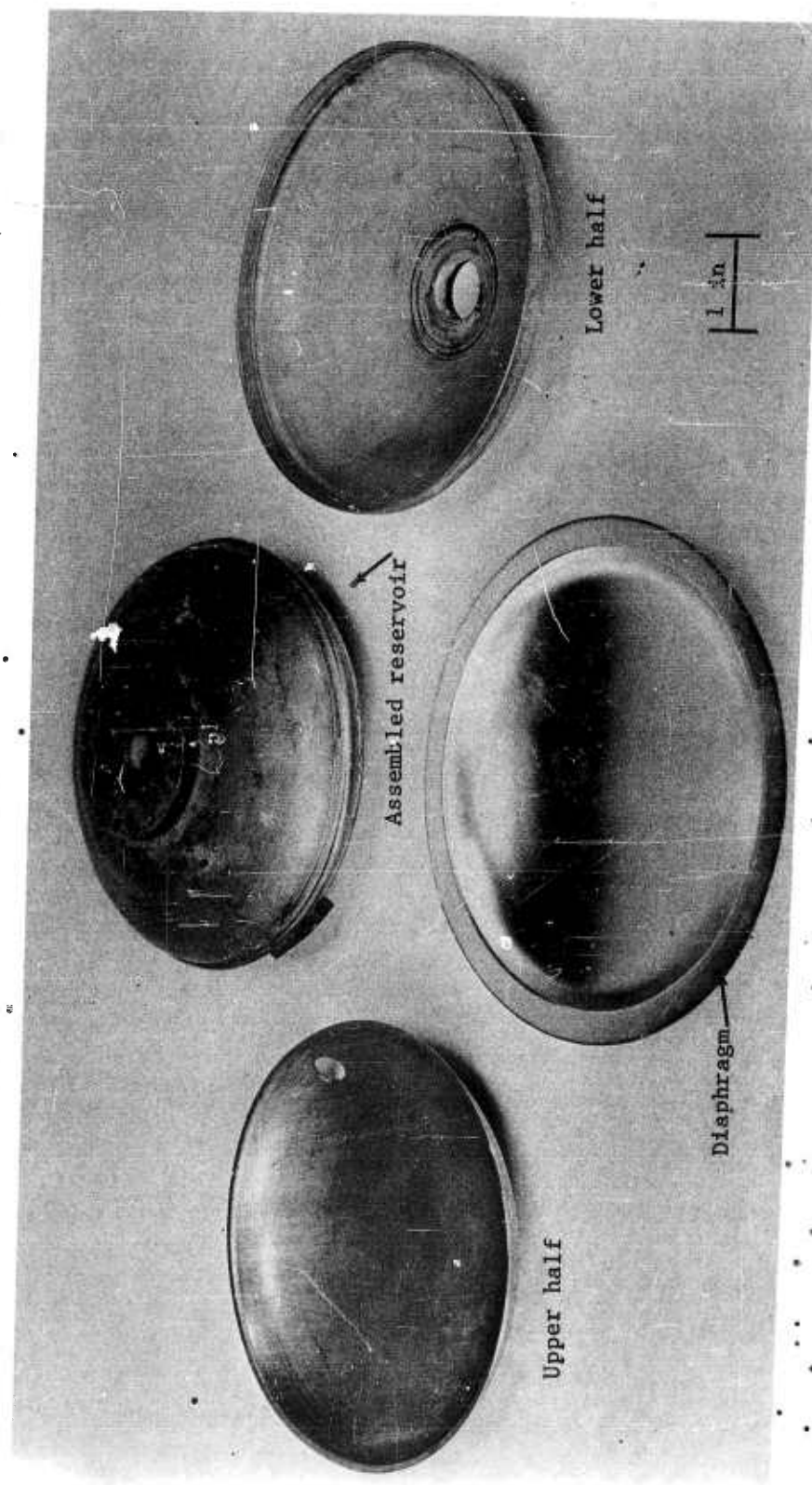


Figure 1. Reservoir components.

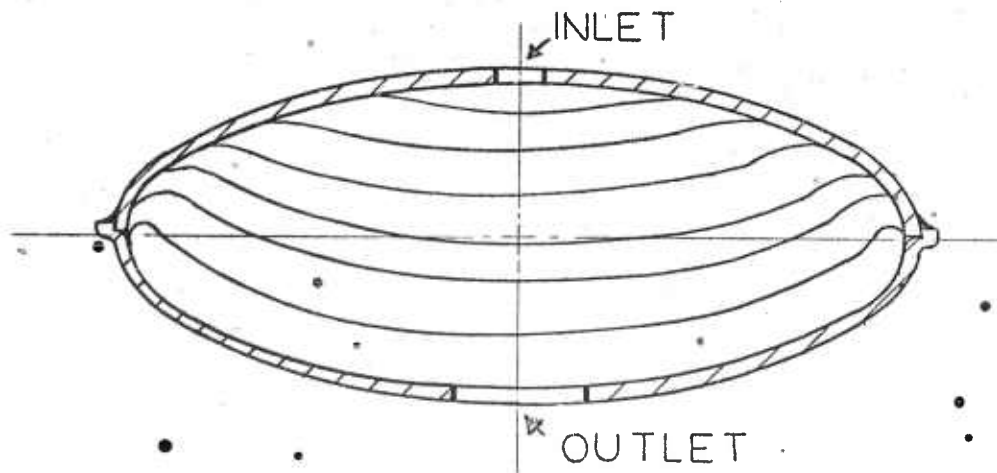
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center (fig. 2). This improper folding results in sharp creases and occasional fracture of the diaphragm, particularly after extreme vibration (ref 2). A highly stressed point where two creases had intersected is shown in figure 3. A failure zone is shown in figure 4. These 10X microphotographs were made of dissected reservoirs taken from expended batteries. Careful examination under higher magnification showed that the failure is entirely mechanical and is not caused by local corrosive action or foreign inclusions (ref 3). Figure 5 shows the location with respect to the gas inlet of diaphragm failures found in 15 batteries from a group of 30 in a recent laboratory test (ref 4).

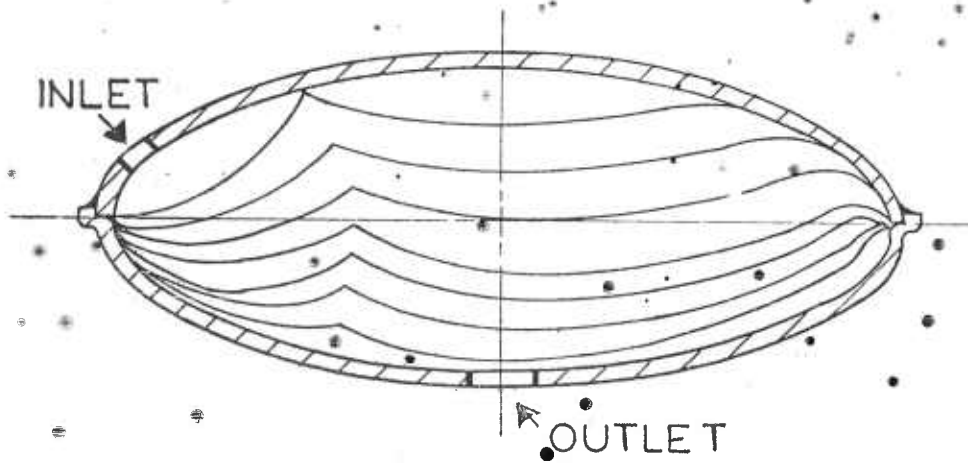
When fractures of sufficient size occur, gas can enter the liquid side of the reservoir, mix with the electrolyte, and pass into the cell pack. Pressures in the system become equalized before all of the electrolyte has been forced from the reservoir and the flow stops thereby starving the cells. (The system is closed and the final pressure in the cells is about 45 psig.) Figures 6 and 7 show reservoirs from battery failures. The lower halves have been removed to expose the diaphragms. Note the relatively undisturbed diaphragm in figure 6. This indicates that failure occurred immediately after activation allowing the gas to escape into the liquid side with little diaphragm movement. The failure in figure 7 occurred later after considerable diaphragm displacement took place. Note the many zones of high stress in figure 7. Diaphragms that do not develop cracks bottom against the lower half of the reservoir. The cell discharge performance is reduced in proportion to the volume of unused electrolyte. This is particularly evident at low ambient test temperatures because (1) more electrolyte is needed by the cells and (2) less heat is carried into the cells from the heat exchanger. When 20 percent or more of the electrolyte remains in the reservoir, the battery cannot deliver the required electrical output at low temperatures.

It is obvious that the battery performance is position-sensitive when the diaphragm fails. When the reservoir exit is down with respect to gravity, the electrolyte and activating gas will not mix. When the exit is up, very little electrolyte will be forced out since the gas will reach the exit first. In intermediate positions, the battery performance will be marginal to unsatisfactory. In actual field use, the battery is activated in a zero gravity field (free flight), and those with diaphragms that fail upon activation will exhibit a performance similar to that in the intermediate positions in the laboratory, i.e., marginal to unsatisfactory (ref. 5). These assumptions were borne out by tests in which the diaphragms had been cut before activation. When the diaphragms do not fail, the position at activation is immaterial.

In order to study the activating mechanism and to determine the cause of diaphragm failure, a comprehensive experimental program was planned. The results of this work, now essentially complete, are reported here. Approximately 60 experiments with actual and simulated activator parts were performed, and the results are discussed below.



(a) Proper diaphragm inversion.



(b) Actual diaphragm inversion.

Figure 2. Proper diaphragm inversion and actual inversion.

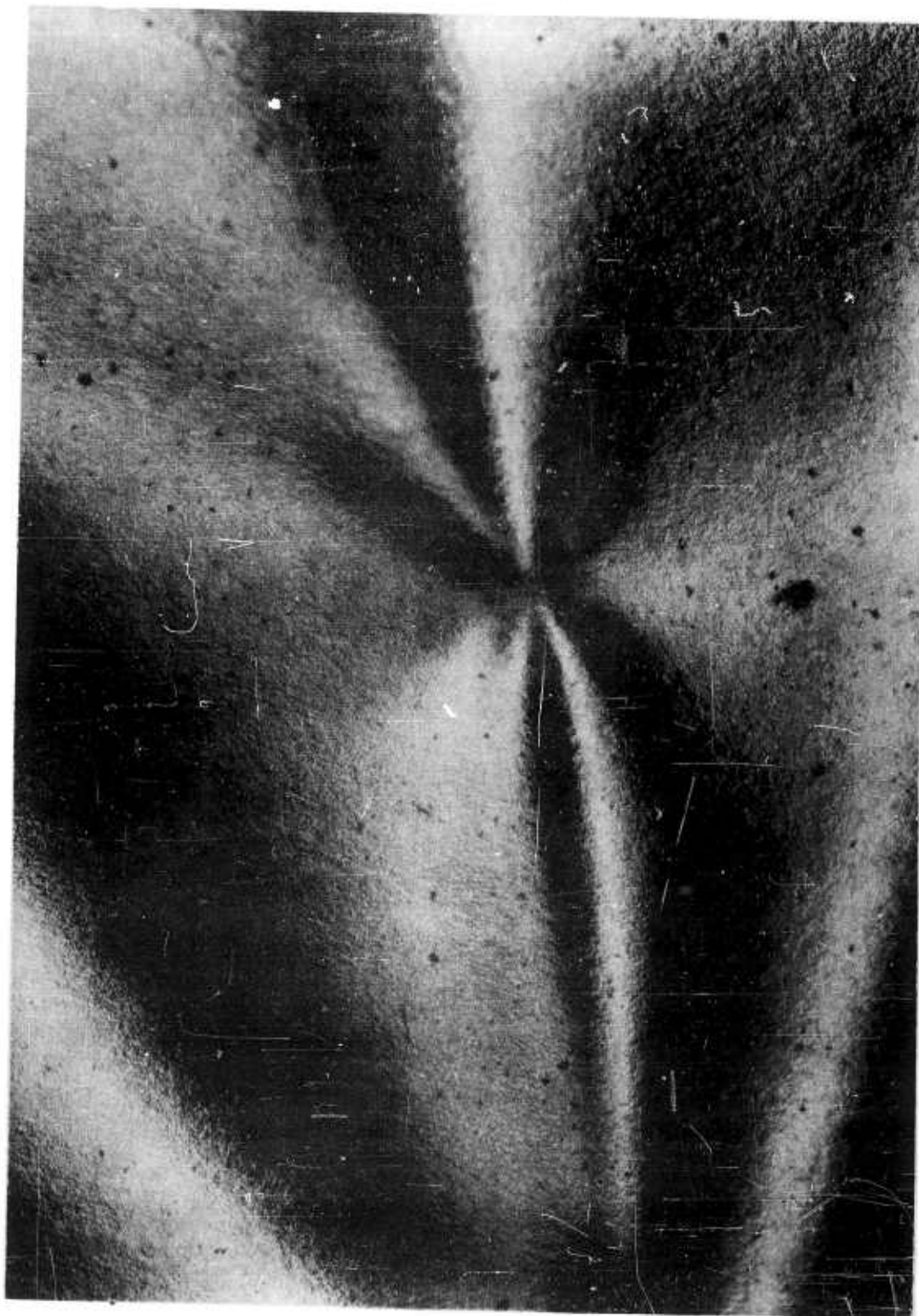


Figure 3. Microphotograph of stressed point in diaphragm - 10X. 998-61



Figure 4. Microphotograph of failure zone in diaphragm - 10X.

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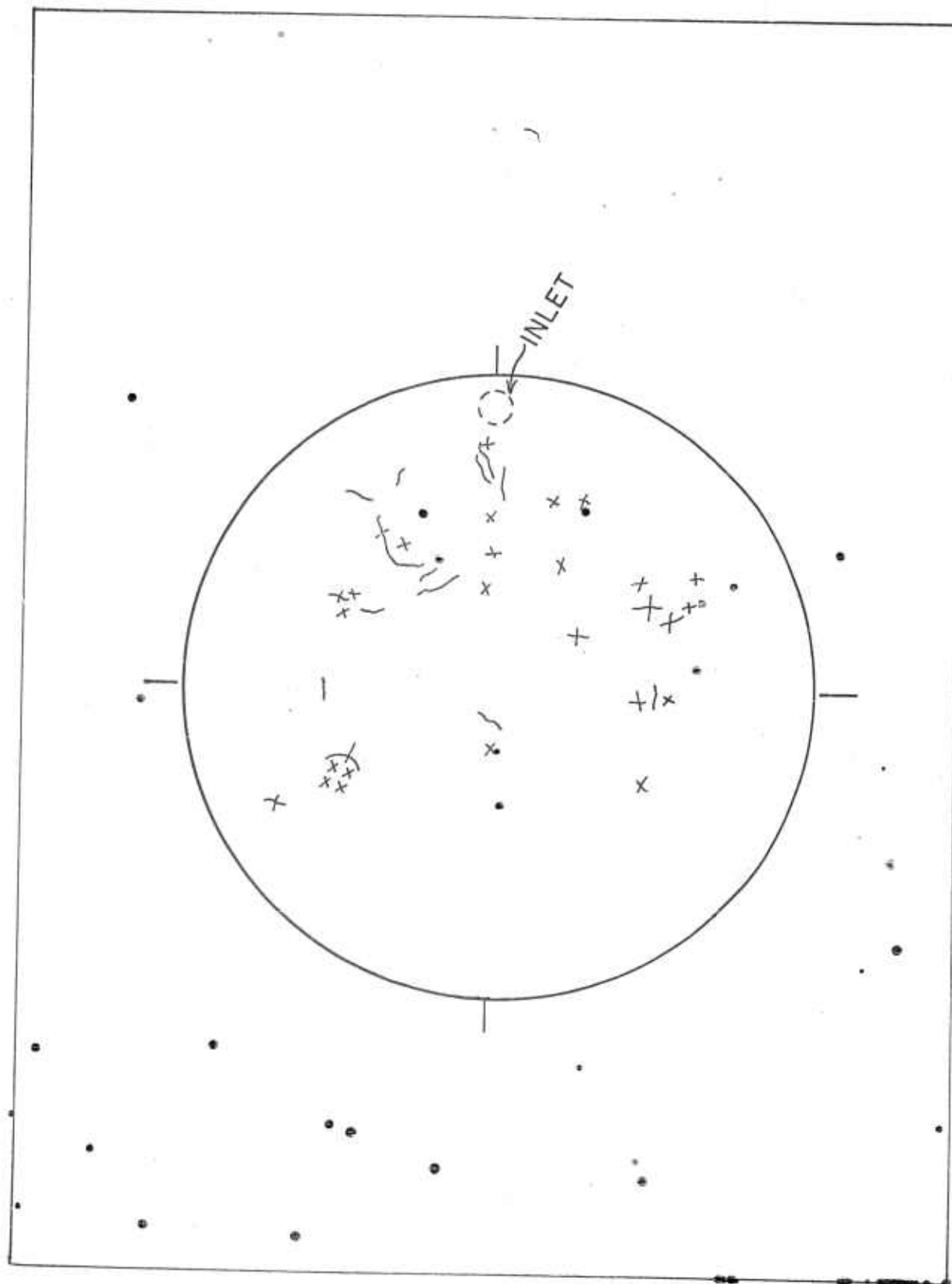


Figure 5. Locations of diaphragm failures compiled from 15 battery post-mortem examinations.

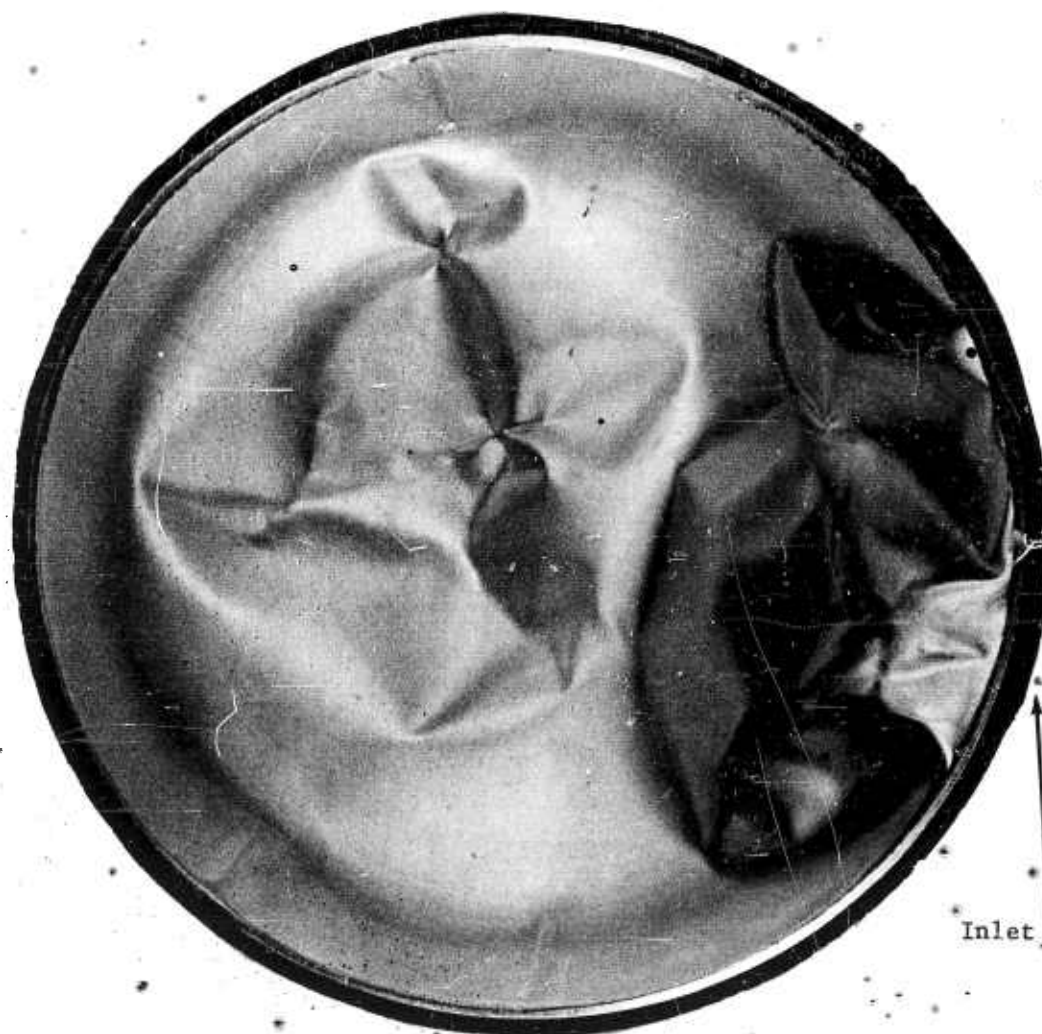
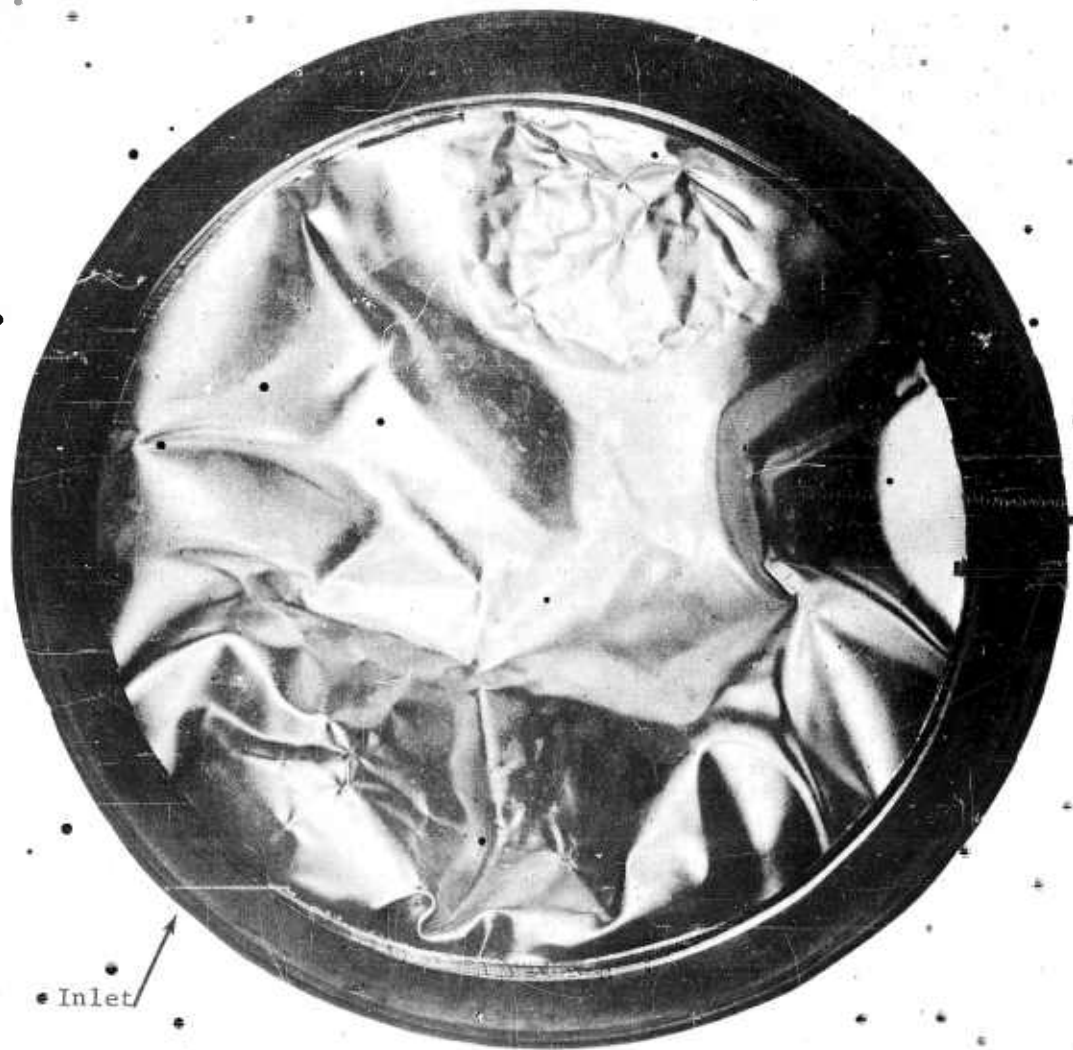


Figure 6. Dissected reservoir showing diaphragm failure. 1. 1638-60



163 -60

Figure 7. Dissected reservoir showing diaphragm failure, 11.

2. EXPERIMENTAL PROCEDURE

So that the motion of the inverting diaphragm could be studied, a transparent reservoir was constructed to permit high-speed motion picture photography. As the program progressed, several modifications in the experimental setup were made. The test devices are discussed below.

2.1 Setup A. Two lucite discs, 7.50 in. in diameter and 2.0 in. thick were constructed with one face of each machined to the same curvature as the inner surfaces of the reservoir (fig. 8). Inlet and outlet holes were drilled, and suitable fittings were attached. (Several inlets are shown in figure 8; only one was used at any one time and the unused ports were blocked.) The diaphragm is clamped by its rim between the flat surfaces of the lucite discs and rests in the upper half of the simulated reservoir.

The simulated reservoir would be filled with water or a potassium tartrate solution of the same specific gravity as the potassium hydroxide solution, 1.32. Potassium hydroxide (KOH) was not used because of the hazard to the eyes and skin of laboratory personnel; some leakage generally occurred during the tests. The exit port is sealed by a 2-mil silver sheet, gaskets, and a pin-strainer assembly exactly as in the battery. In this setup the diaphragm was photographed from the gas side. Tubing from a used heat exchanger connects the reservoir to the electrolyte receiver simulating a cell pack. A multihole nozzle simulates the constrictions within the cell pack manifold. The volume of the receiver is the same as the free volume of the cell pack, 380 cc.

The activator consists of a U-tube from a battery modified by fittings and solenoid valves for rapid valving of a fixed volume of gas at an adjusted initial pressure. A second system uses the battery activator that contains a sealed volume of gas under pressure. Electrically detonated squibs release the gas by rupturing diaphragms near the ends of the U-tube.

2.2 Setup B. To simulate the reservoir more closely, the top lucite disc was replaced by a metal upper half. Figure 9 shows the upper half with an activator mounted on it. Photography now had to be from the liquid side. The exit port was moved from the center of the lower half to one edge, out of the field of view (fig. 10 and 11). The metal electrolyte receiver was replaced with a transparent one so that flow rates could be measured. A clock was included, and the diaphragm, electrolyte receiver, and clock were photographed together. Films made with this setup were of higher quality because smoke from the squibs could not obscure the view of the diaphragm.

2.3 Setup C. A third setup was used so that photographs of diaphragms assembled in actual reservoir shells could be made. Reservoirs from unfired batteries were modified by removing most of the lower half. They would then be placed in the transparent lower half. Sealing was accomplished by O-rings while the reservoir was held in place by a rigid ring (fig. 12).

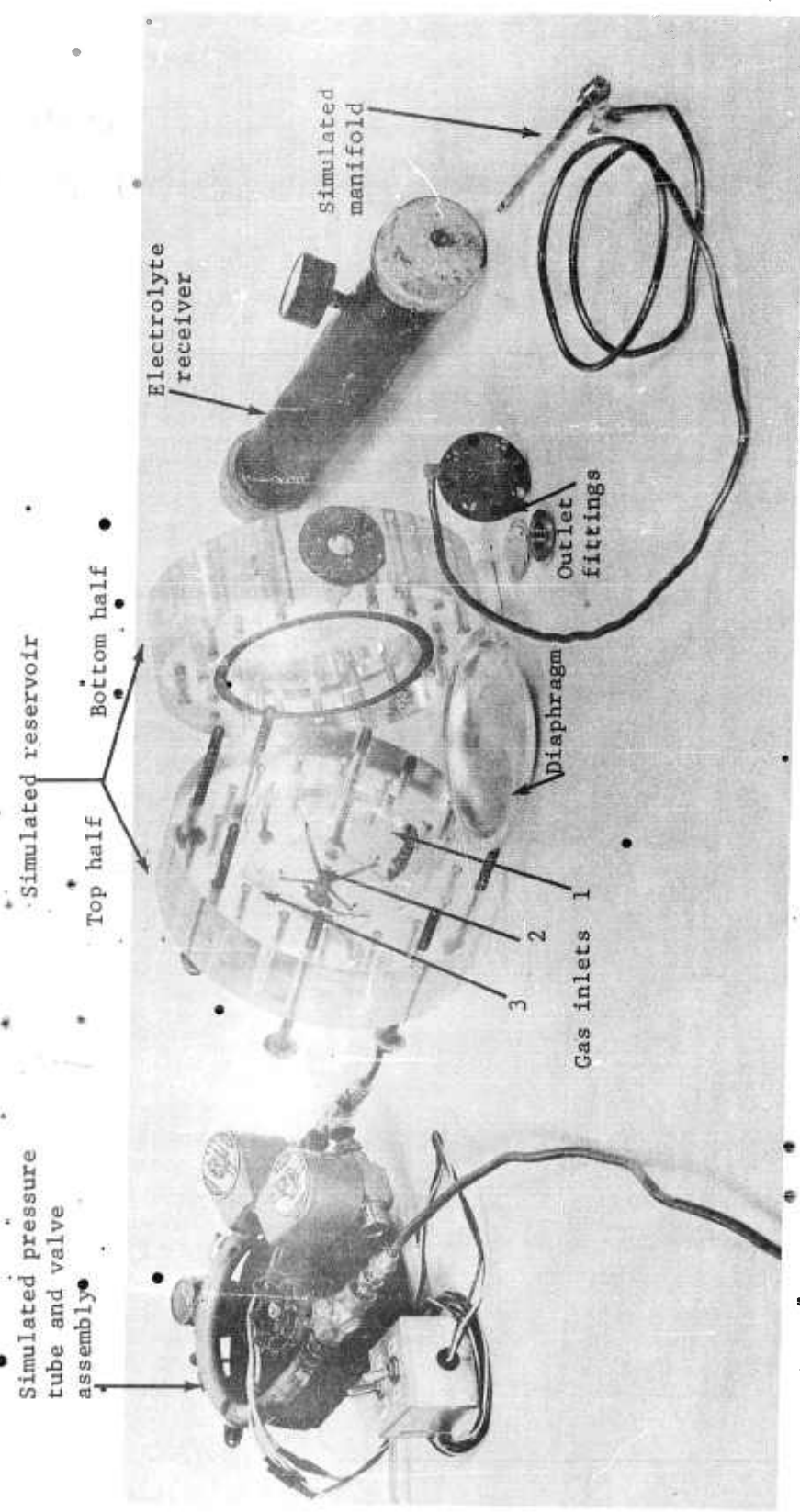
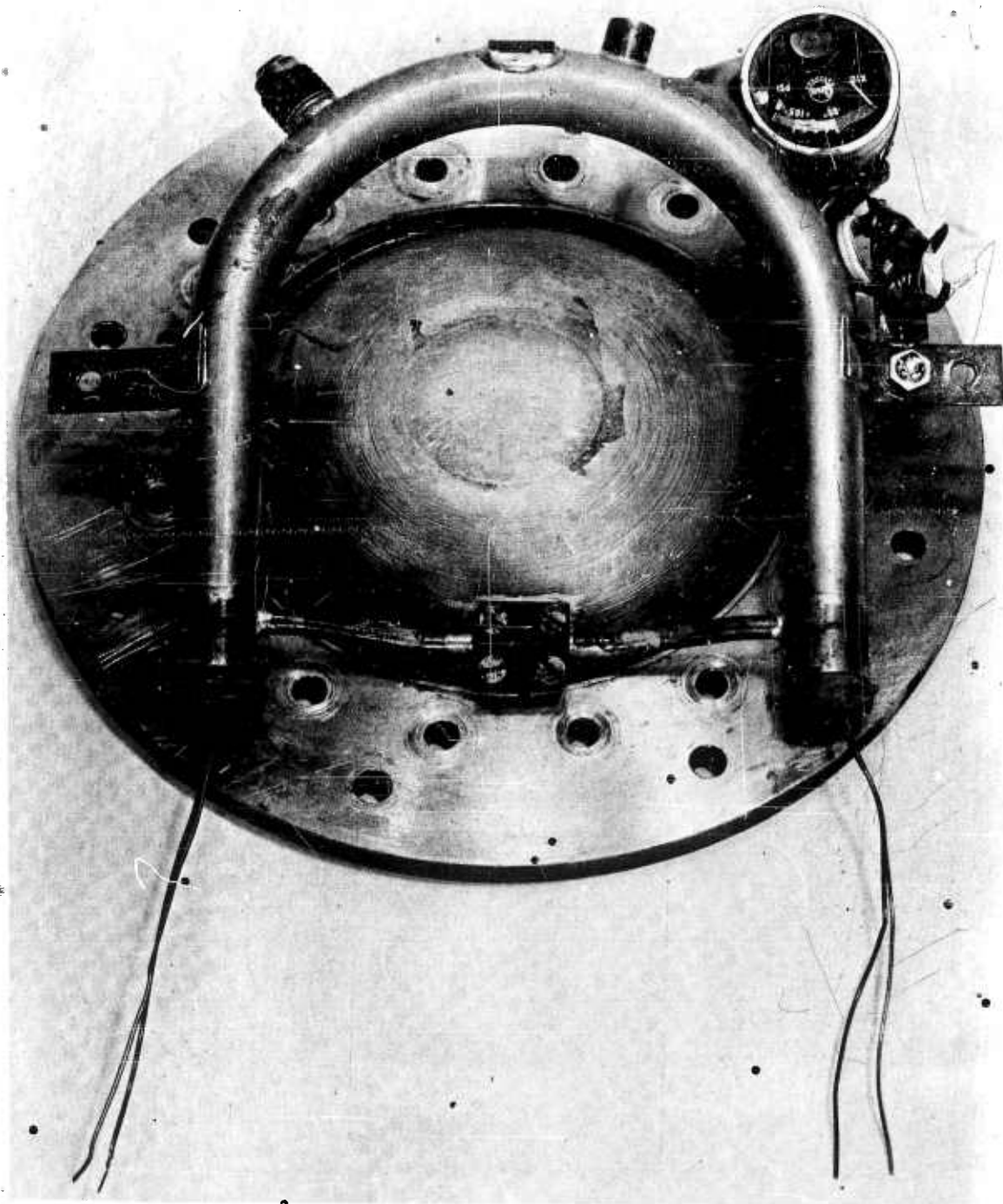


Figure 8. Experimental setup A, disassembled.



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Figure 9. Top half of simulated electrolyte reservoir, with battery activator (setup B).

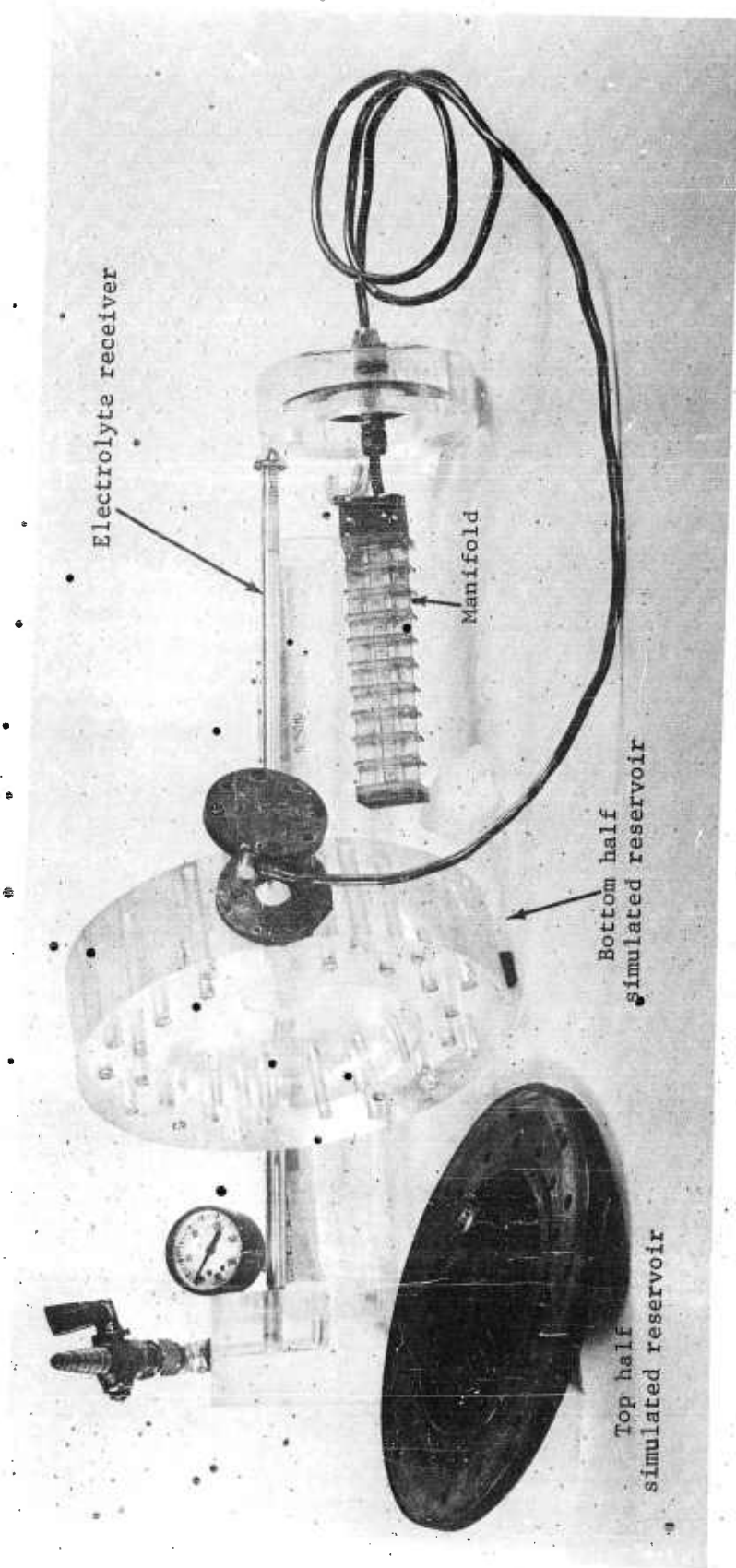


Figure 10. Experimental setup B, disassembled.

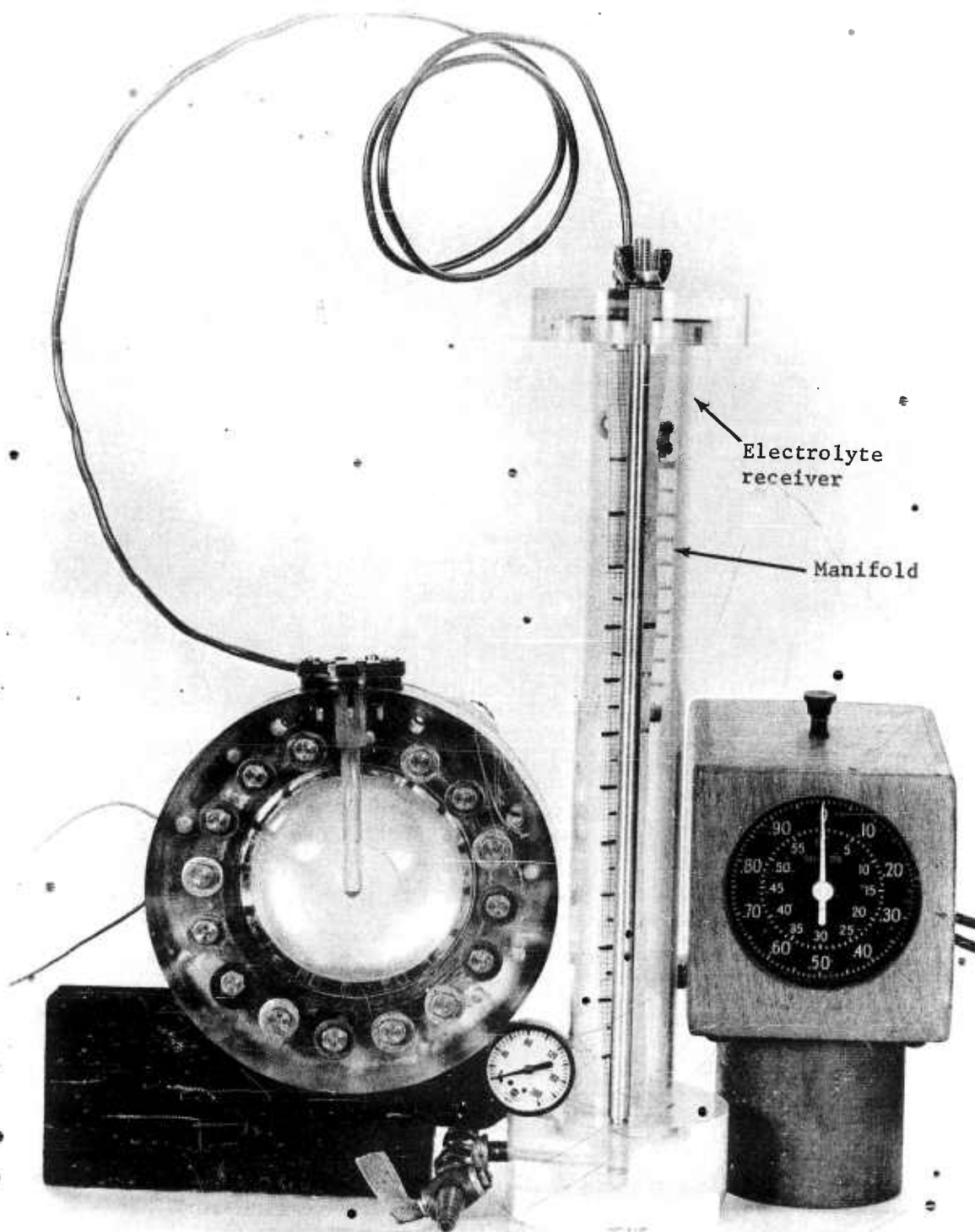


Figure 11. Experimental setup B, assembled.

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Outlet
fitting

Bottom half
simulated
electrolyte
reservoir

Copper
gasket

Electrolyte
reservoir,
bottom half
removed

"O" Ring

Clamp
ring

Figure 12. Experimental setup C.

3469-60

A number of experiments were performed in which the diameter of the gas inlet was reduced. The connector on the activator (fig. 9) was milled and a small brass disc containing the orifice(s) was pressed into the recess. The purpose of this modification was to reduce the extremely high-pressure blast of the activator squibs. The peak pressure at the gas inlet before diaphragm and electrolyte displacement takes place is calculated to be 7000 psi. This pressure is quickly dissipated as the gas cools and expands into the reservoir, but not before the diaphragm is stressed and begins to fold improperly.

Approximately 60 tests were made with the experimental setups described. Of these, 41 were photographed on 16-mm film at speeds of 120 to 1500 frames per second. The films of the early tests were of rather poor quality for a number of reasons, but with the experience gained, the later films were excellent, showing, when projected at normal speeds, the folding of the diaphragm in ultra slow motion.

Frames from the films of 5 tests are shown in figures 13, 14, and 15. With the exception of test No. 3 (fig. 15), the tests were all filmed from the liquid side. Test No. 3 shows how the smoke from the squibs obscures part of the diaphragm when the test is filmed from the gas side. Test No. 18, (fig. 13), is typical of the folding action when squibbed activators are used. The initial movement is at the point of gas entry and is followed by inversion near the center. Figure 14, test No. 8, shows proper folding. Here pressurized nitrogen at 500 psi was valved into the reservoir through the inlet at the edge of the reservoir. In figure 15, test No. 42 is of interest because it shows at very high speed the fluttering of the diaphragm caused by the squib detonation (note the temporary blisters in the upper right side). Test No. 42 was performed with the squibbed activator, but the gas inlet diameter was reduced to 0.040 in. The folding is proper.

Figure 16 shows one unused and three inverted diaphragms. The dark smudges show the position of the gas inlet before inversion. The smoothness is a function of freedom from liquid leaks during the test. The diaphragms were used in tests 52, 51, and 53, respectively.

The tests are listed in table 1, not chronologically, but according to the test setup and modification used. Table 2 lists, in detail, the tests, the serial numbers, and the differences of each test. Table 3 shows the results of the film study in regard to proper or improper folding of the diaphragm. The combined results of all tests are itemized below.

3. TEST RESULTS

(1) With one exception, the diaphragm did not fail in any of the tests, whether it was used as it came from the manufacturer or whether it was mistreated by being scratched, heated, soaked in hot KOH, vibrated, or contaminated with mercury. The one failure occurred in test No. 37. A slit 1/8 in. long had been cut at a point about 1 in. from the edge and

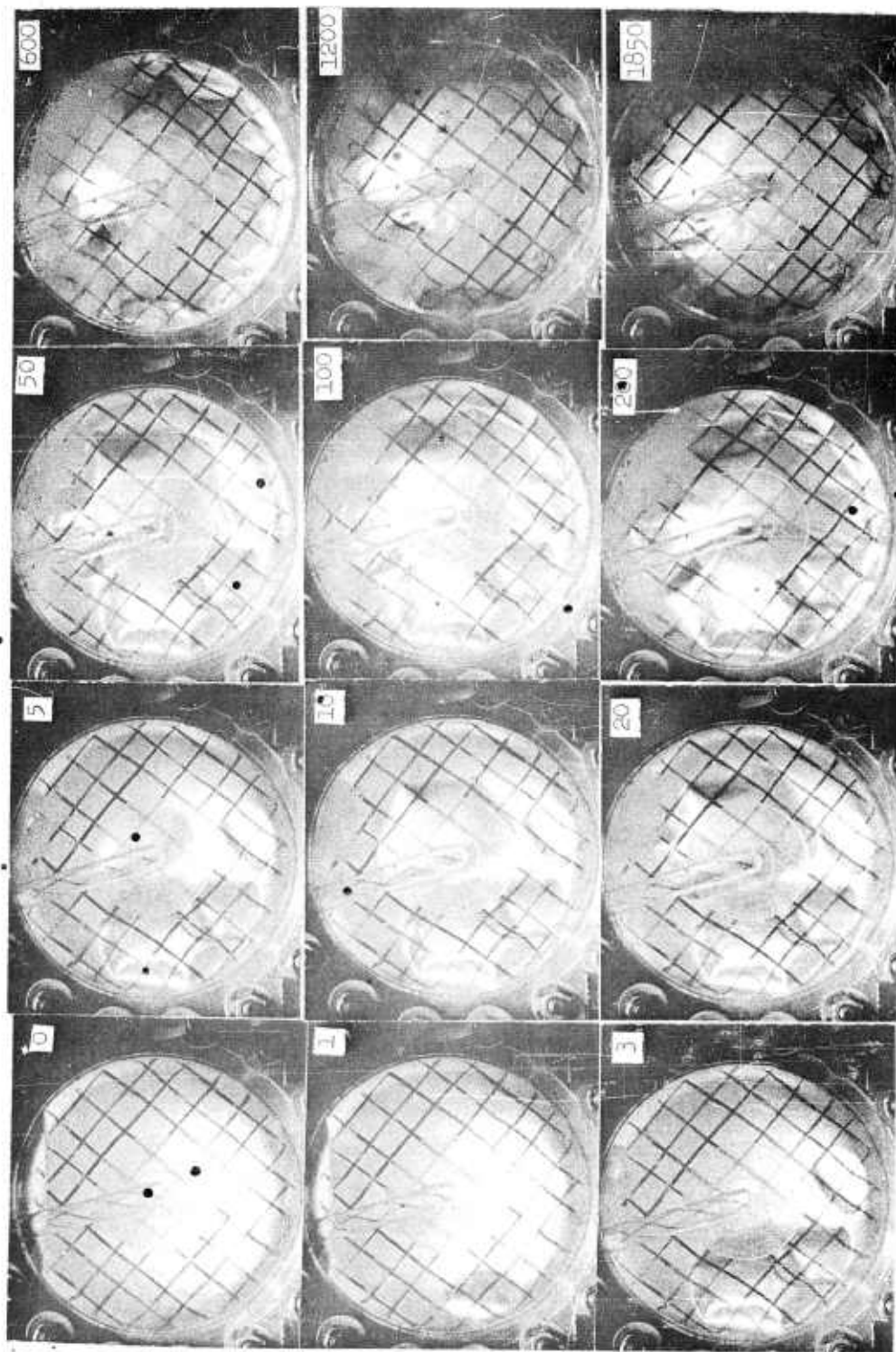


Figure 13. Folding sequence, test 18, 128 frames per second. 1000-61
 (Numerals identify the frame number.)

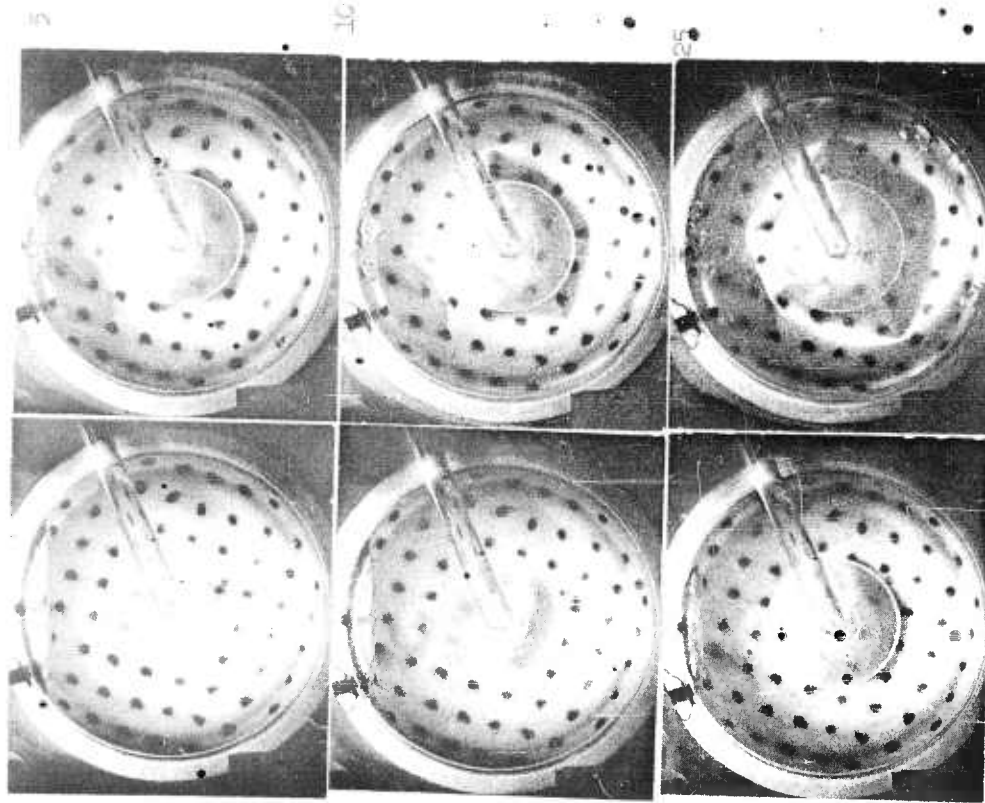


Figure 14. Folding sequence, test 8, at 128 frames per second.
(Numerals identify the frame number.)

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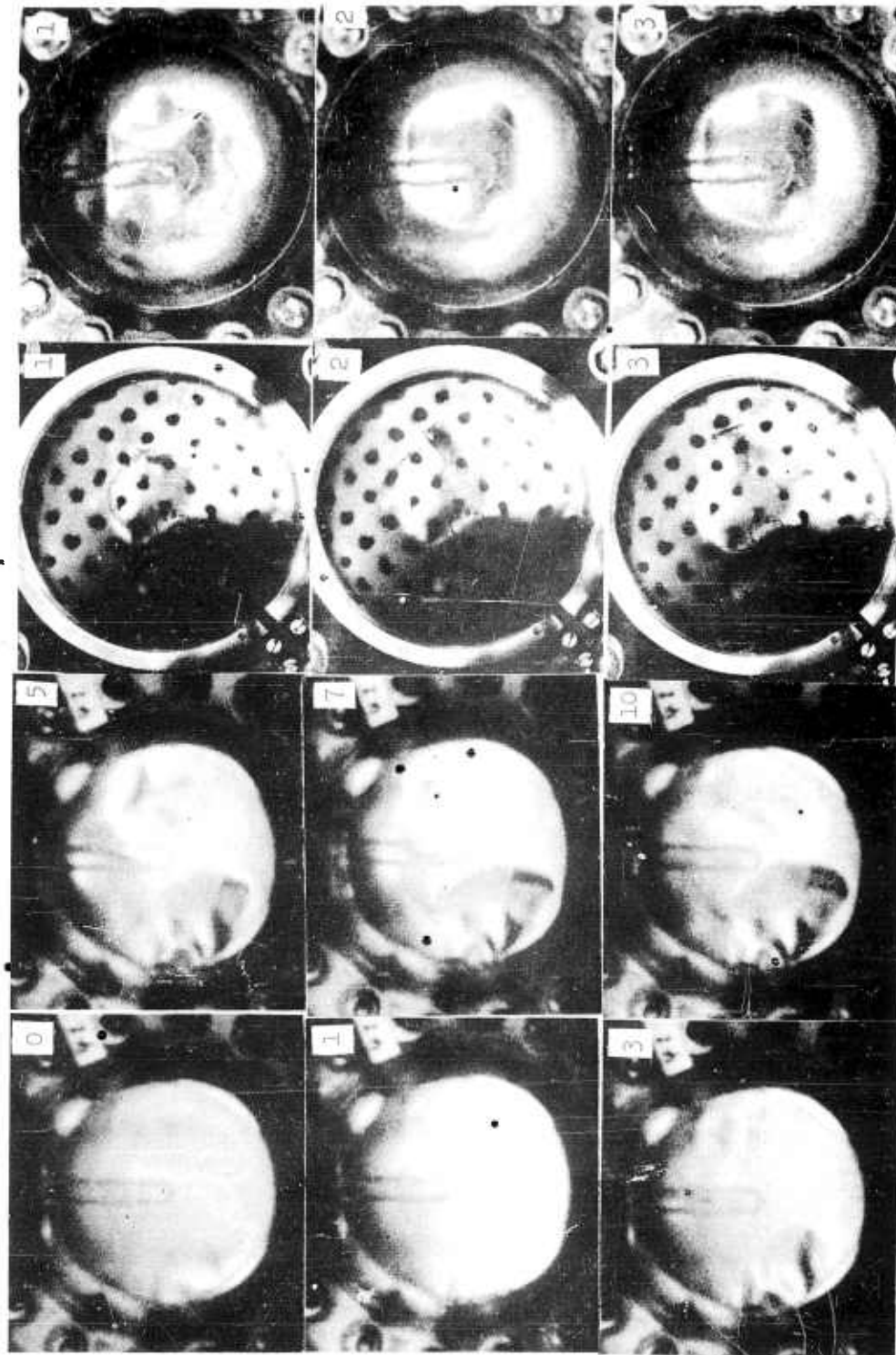


Figure 15. Folding sequences, tests 42, 3, and 53 taken at 1500, 400, and 400 frames per second.
 (Numerals identify the frame number.)

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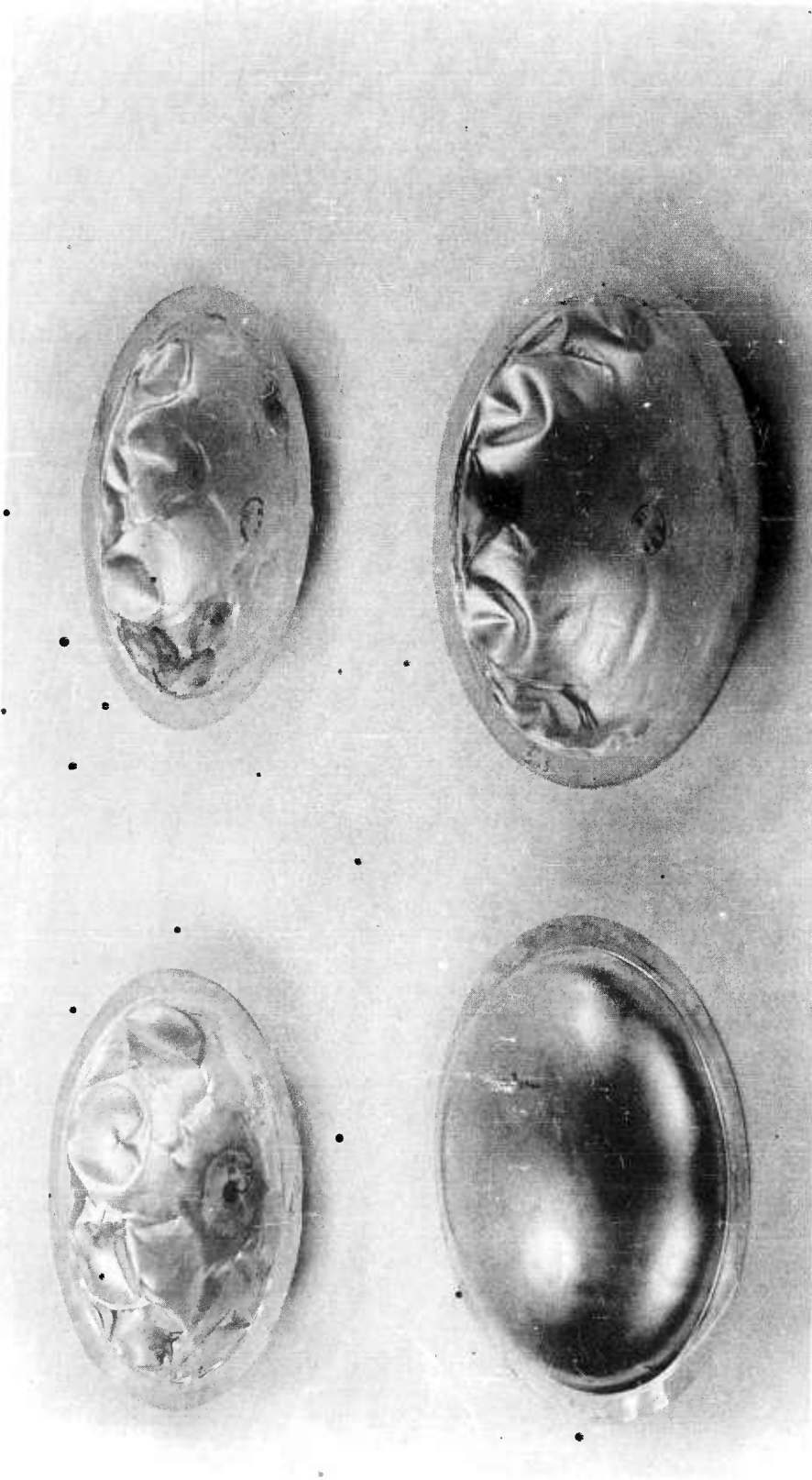


Figure 16. Samples of diaphragms before and after folding.

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Table 1. Tests Listed According to Experimental Setup

Setup	Reservoir	Pressure source	Gas inlet		Test numbers*
			Location	Size	
A1	Lucite top and bottom	Gas bottle, valves	Edge	0.21-in. diam	<u>1</u> , <u>5</u> , <u>6</u>
A2	Lucite top and bottom	Activator, squibs	Edge	0.21-in. diam	<u>2</u> , <u>3</u> , <u>4</u>
A3	Lucite top and bottom	Activator, squibs	Center	0.21-in. diam	<u>52</u>
A4	Lucite top and bottom	Activator, squibs	1 1/4 in. from center, equally spaced	Four 1/16-in. holes	<u>50</u> , <u>51</u>
A5	Lucite top and bottom	Gas bottle, valves	1 1/4 in. from center, equally spaced	Four 1/16-in. holes	<u>49</u>
B1	Metal top, lucite bottom	Gas bottle, valves	Edge	0.21-in. diam	<u>8</u> , <u>9</u> , <u>12</u> , <u>26</u> , <u>26A</u> , <u>43</u> , <u>44</u>
B2	Metal top, lucite bottom	Activator, squibs	Edge	0.21-in. diam	<u>10</u> , <u>11</u> , <u>13</u> , <u>14</u> , <u>15</u> , <u>16</u> , <u>17</u> , <u>18</u> , <u>19</u> , <u>20</u> , <u>21</u> , <u>22</u> , <u>23</u> , <u>24</u> , <u>25</u> , <u>27</u> , <u>28</u> , <u>29</u> , <u>30</u> , <u>37</u> , <u>39</u> , <u>40</u> , <u>46</u> , <u>47</u> , <u>48</u> , <u>54</u>
B3	Metal top, lucite bottom	Activator, squibs	Edge	One 1/16-in. hole	<u>31</u> , <u>33</u> , <u>45</u>
B4	Metal top, lucite bottom	Activator, squibs	Edge	Six 1/16-in. holes	<u>7</u>
B5	Metal top, lucite bottom	Activator, squibs	Edge	Four 1/32-in. holes	<u>32</u> , <u>34</u> , <u>41</u>
B6	Metal top, lucite bottom	Activator, squibs	Edge	One 0.040-in. hole	<u>53</u> , <u>55</u> , <u>56</u> , <u>57</u> , <u>58</u> , <u>59</u>
C1	Battery reservoir, metal bottom removed and replaced by lucite	Activator, squibs	Edge	0.21-in. diam	<u>35</u> , <u>36</u>
C2	Battery reservoir, metal bottom removed and replaced by lucite	Activator, squibs	Edge	Four 1/32-in. holes	<u>42</u>

* Underlined numbers indicate that motion pictures were taken.

Table 2. Differences in Tests by Setup and Test Number

Setup	Test No.*	Differences or special features
A1	<u>1</u>	6-in. tubing between valve and gas inlet.
	<u>5,6</u>	2-in. tubing between valve and gas inlet.
A2	<u>2,3,4</u>	First tests with battery activator; filmed from gas side.
A3	<u>52</u>	Gas introduced at center of reservoir.
A4	<u>50,51</u>	Gas introduced through 4 holes near center.
A5	49	Same as A4 but bottled gas used instead of battery activator.
B1	<u>8,9,12</u>	First use of metal upper half of reservoir.
	* <u>26</u>	No liquid in reservoir.
	26A	Diaphragm of test 26 inverted 3 times by low pressure gas, then used in regular test. Pinholes were present but no further tearing occurred during test.
	<u>43,44</u>	First use of transparent electrolyte receiver.
B2	<u>10,11,13</u>	Routine tests, in effort to obtain a failure.
	<u>14,15,16</u>	
	<u>17,18</u>	Battery activator heated to increase pressure to that normal at 160°F ambient. (Reservoir horizontal, gas inlet on bottom in tests 19,20,21,22,23,24,25,27,28,39, and 40; in all other tests diaphragm and reservoir in vertical position.)
	19	Routine.
	20	Diaphragm had not been annealed after it was formed.
	21	Diaphragm from current manufacture.
	22	Diaphragm had been contaminated with mercury for 24 hr.
	23	Diaphragm had a flaw in center from forming operation. It did not fail upon inversion.
	24	Diaphragm soaked in KOH at 160°F for 100 hr.
	25	Diaphragm had been heated to 1100°F around edges (simulating brazing operation of reservoir assembly).
	<u>27</u>	Diaphragm soaked in KOH at 160°F for 180 hr, then scored on both sides with sharp, pointed tool.
	28	Diaphragm in filled reservoir subjected to flight vibration at 5 g.
	29	Same as test No. 28 but at 15 g.

*Underlined numbers indicate that motion pictures were taken.

Table 2. Differences in Tests by Setup and Test Number (Continued)

Setup	Test No.*	Differences or special features
B2	<u>30</u>	Diaphragm had been dimpled inward at gas inlet point three times, then smoothed and tested.
	<u>37</u>	1/8-in. slit cut in diaphragm one inch from edge opposite gas entry point. After test, a second 1/8 in. crack found near gas entry point. Neither opening prevented adequate pumping.
	<u>39</u>	1/8-in. X cut in diaphragm near inlet. Pumping incomplete. Diaphragm horizontal, gas inlet down.
	<u>40</u>	Diaphragm of test no. 39 reversed under low pressure and reused. Pumping incomplete as in 39.
	<u>46</u>	Special test with annular groove in diaphragm near its edge. Folding started in center but was not completed due to stiffness at groove.
	<u>47</u>	Routine.
	<u>48</u>	Minimum pressure (360 psi) in activator.
	<u>54</u>	Routine.
B3	<u>31, 33, 45</u>	Reduced gas inlet diameters. (See table 1.)
B4	<u>7</u>	Reduced gas inlet diameters. (See table 1.)
B5	<u>32, 34, 41</u>	Reduced gas inlet diameters. (See table 1.)
B6	<u>53, 55, 56, 57, 58, 59</u>	Reduced gas inlet diameters. (See table 1.)
C1	<u>35</u>	Reservoir from old unused battery. Pinhole noted in diaphragm. Pumped properly.
	<u>36</u>	Reservoir from old unused battery. Diaphragm appeared normal.
C2.	<u>42</u>	Reservoir from unused battery. Gas inlet diameter reduced for test.

* Underlined numbers indicate that motion pictures were taken

Table 3. Analysis of Films of Diaphragm Movement

Type activation	Initial pressure	Inlet location	Inlet size restriction	Setup	Tests in which folding began at edge	Tests in which folding began at center
Valved	8 - 500 psi 5,43,44 - 750 psi 6, 9,26 - 1000 psi	Edge	None	A1 B1	- 43	5,6 • 8,9,26,44
Squib released	48 - 360 psi 17,18 - 650 psi remainder - 525 psi	Edge	None	A2 B2 C1	2,3 10,11,13,14,15,16,17 18,27,40,47,48,54 • 35,36	46 (annular groove)
Squib released	all - 525 psi	Edge	One 1/16-in. hole Six 1/16-in. holes Four 1/32-in. holes Four 1/32-in. holes One .040 hole	B3 B4 B5 C2 B6	45 7 32, 34, 41 42 56,57,58 (small dimple)	33 - - - 53,55,59
Squib released	525 psi	Center	None	A3	-	52
Squib released	both - 525 psi	1 1/4 in. from center equally spaced	Four 1/16-in. holes	A4	-	50,51*
Valved	750 psi	1 1/4 in. from center equally spaced	Four 1/16-in. holes	A5	-	49

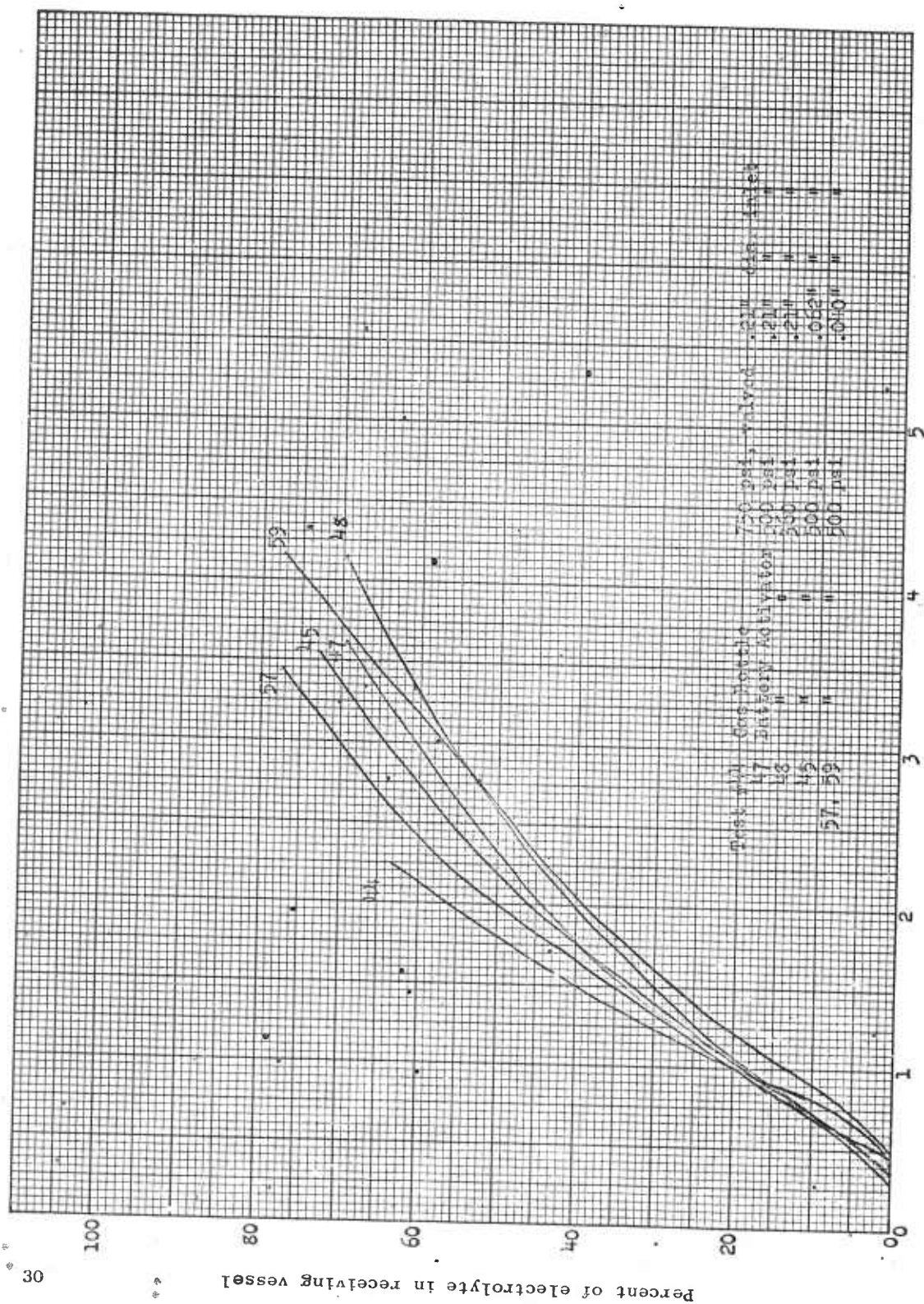
was placed so that the cut was opposite the inlet point. After the test, a second slit was found near the inlet point. Neither opening admitted enough gas to prevent the complete inversion of the diaphragm. The following hypotheses are offered to explain the failures experienced in batteries but not duplicated in these tests:

- (a) The diaphragm used in these tests may be of higher quality (more ductile, freer of large grain growth, wrinkles, and mechanical strains) than those in recently produced batteries.
 - (b) The stresses from the high-pressure shock by the detonating squibs are not truly simulated in these tests.
 - (c) The combined effects of improper heat treatment of the silver battery vibration preconditioning, long contact with the electrolyte, folding at low ambient temperatures, contamination during manufacture, and mechanical strains set up during assembly may have induced weaknesses that caused failures upon battery activation.
- (2) The diaphragms do not fold properly when battery activators (with squibs) are used. This is caused (a) by the high-pressure shock from the exploding squibs and (b) by the location of the point of gas entry. Improper folding is evidenced by the films and by post mortem examinations of reservoirs from batteries with diaphragm failure.
- (3) Diaphragms do fold properly when (a) activator squibs are not used (gas valved from pressurized U-tubes), (b) when the point of gas entry is near the axis of the reservoir, and (c) when the blast effects are reduced by sufficient restriction of the gas inlet cross section.
- (4) The electrolyte flow rate is fairly independent of the pressure of the activating gas and whether or not activating squibs are used (fig. 17). The flow rate is controlled by the restriction of the manifold holes and the electrolyte viscosity (no low temperature tests were made here). The electrolyte reaches the cell pack in about 0.5 sec, flows at a reasonably constant rate, and the flow is completed in about 6 sec.

4. RECOMMENDATIONS

The following recommendations, based upon the results of these tests, battery post-mortem examination, and mechanical engineering judgment, are offered for a modification of the design to reduce failures of the reservoir diaphragm:

- (1) Move the point of gas entry into the reservoir from the edge toward the axis of the reservoir to allow the diaphragm to fold properly. This could be done without changing the container dimensions if the gas inlets are arranged as in Setup A4 and A5. A single inlet on the axis would require a substantial increase in one dimension.



Seconds after initiation.
Figure 17. Electrolyte flow rates with different activators.

(2) Reduce the cross section of the gas inlet from 0.035 in.² to 0.0012 in.² to reduce the high pressure blast from the squibs. Incorporate a strainer in the gas passageway to prevent the possibility of blocking the smaller gas inlet with squib residue.

(3) Use more uniform reservoir parts to prevent wrinkling or stressing the diaphragms during assembly.*

(4) Extend the study of silver metallurgy to guarantee against low tensile strength and to increase the ductility of the diaphragm.*

These design changes would prove to be simple, requiring negligible increase in costs and no changes in the rest of the system, already proved in extensive evaluation tests. Before units of a new design could be used to replace those now in the field, an environmental evaluation program for testing the new design should be conducted.

5. REFERENCES

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5. DOFL Report R-330-50-11, "Laboratory Performance of PS502 and PS502A Power Supplies -- Third Report," G. Scillian, 11 July 1960.

* Progress has been made in these fields and is to be reported at a later date.

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The motion of the pumping diaphragm in the electrolyte reservoir of the PS502-502A power supply was studied during its operation by means of transparent models and high-speed motion picture photography. The primary purposes of the investigation were to determine the causes of occasional diaphragm failure that has led to electrical failure of the battery and to find means of eliminating the causes. The failures were found to be due to excessive mechanical stress caused, in turn, by (1) high-pressure shock from the detonating squibs used to release the stored pressurized gas and (2) improper folding of the diaphragm during activation. Recommendations are given for the improvement of design and performance.			The motion of the pumping diaphragm in the electrolyte reservoir of the PS502-502A power supply was studied during its operation by means of transparent models and high-speed motion picture photography. The primary purposes of the investigation were to determine the causes of occasional diaphragm failure that has led to electrical failure of the battery and to find means of eliminating the causes. The failures were found to be due to excessive mechanical stress caused, in turn, by (1) high-pressure shock from the detonating squibs used to release the stored pressurized gas and (2) improper folding of the diaphragm during activation. Recommendations are given for the improvement of design and performance.		
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